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# A Comparative Study Between Nanocrystalline and Polycrystalline CdS Semiconductor Films

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**Abstract:** A chemical bath deposition technique was used to prepare nanocrystalline and polycrystalline CdS semiconductor films on glass/metal substrates at 28 $^0$C and 80 $^0$C respectively using 1M $CdSO_4$, 1M thiourea and 2M $NH_4OH$. The time duration for preparing bulk CdS film was 30 minutes whereas for nanocrystalline CdS film, the deposition time was varied from 2 to 90 minutes. The pH of the solution was also varied for nanocrystalline CdS film. Compositional analysis of the bulk CdS film indicated Cd:S = 50.4:49.6 whereas the nanocrystalline films showed sulfur deficiency. Band gap values were estimated by optical absorption studies and found to be 2.4 eV for bulk CdS whereas for nanocrystalline CdS the band gap changed from 2.40 to 2.99 eV with decreasing time period of deposition. The fundamental absorption edge was seen to shift to lower wavelength for films prepared at lower deposition times in the case of nanocrystalline films. The photo effects were studied in the solar cell configuration as Ti/CdS/$Na_2SO_3$/Pt and the photovoltages were found to increase from the bulk value.

**Keywords:** Cadmium sulfide thin films, optical absorption studies, Rutherford backscattering spectrometry.
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## 1. Introduction

A great deal of research has been done recently by several groups on nanocrystalline semiconductor materials. Group II-VI semiconductor materials such as CdSe or CdS have been intensively used as the model material for the preparation of nanoparticles due to the ease of their fabrication. We were working on polycrystalline CdS films in order to fabricate photoelectrochemical solar cells. Chemical deposition of CdS films and their characterization studies from this

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laboratory have recently been reported [1] by one of us (S.N.S.). While making further investigation in this material, we noticed the fundamental absorption edge to shift to lower wavelength for films prepared at lower deposition time and temperature. This observation motivated us to the present study.

It is now known that nano/small size crystals ($\sim$ a few nm) exhibit the "quantum confinement effect" [2–6]. Nanoparticles possess physical properties that are intermediate between those corresponding to the bulk solid and molecules. When electrons and holes are confined within a small three-dimensional potential well, the continuum of states in the conduction and valence band is broken down into discrete states with an energy spacing, relative to the band edge, which is approximately inversely proportional to the square of the particle size [2]. This leads to new effective band gaps and electrical properties. Nanostructured semiconductor materials have emerged as new materials for possible use in optoelectronics [7].

The following systems, among others, have been used to prepare nano/small crystallites of the desired size: vesicles [8], micelles [9], polymers [10,11], glasses [12,13], zeolites [14,15], and Langmuir-Blodgett film [16]. So in order to study this quantum confinement effect, we have grown CdS films in glass/metal substrates using solution growth method which is cheaper, easier to prepare, and different from other methods. In this paper we present a comparative study between nanocystalline and polycrystalline CdS semiconductor films. A brief description of the experimental methods is given in sec. 2. In sec. 3 we report various results with brief discussion. Finally we conclude by summarizing the essential results in sec. 4.

## 2. Experimental

### 2.1 CdS film preparation

The experimental arrangement consists of a 50 ml beaker containing ammoniacal solution of $CdSO_4$ and thiourea. Various substrates, namely Ti and glass, were polished with fine emery paper, washed, then soaked in 0.5 M NaOH, washed further, etched with dilute $HNO_3$, washed again and finally ultrasonically cleaned in acetone to prepare CdS films. One molar $CdSO_4$ solution and one molar thiourea solution were prepared, each with 5 ml of Millipore Q plus water. Approximately 2M $NH_4OH$ solution was then added to the $CdSO_4$ solution which immediately turned white turbid, presumably forming $Cd(OH)_2$, and when excess $NH_4OH$ was added, the white turbid solution became clear, giving $Cd(NH_3)_4^{2+}$ ions in the solution. Thiourea was added to this clear solution. The total volume of the bulk solution was kept at 35 ml with pH 11.7. Two cleaned substrates held firmly by the substrate holder were immersed into the bulk chemical solution maintained at 80 $^0$C in a constant-temperature bath, and

the deposition was carried out under moderately stirred conditions for 30 min. The CdS film formation mechanism may be assumed to be due to adsorption reaction of $Cd^{2+}$ from $Cd(NH_3)_4^{2+}$ and $S^{2-}$ from the hydrolysis of thiourea. The as-deposited films were thoroughly washed with a fine water jet and dried in air. Same procedure was followed for preparing nanocystalline CdS films by varying temperature, time of deposit and pH of the solution. Thin films prepared in this way were then subjected to different analyses.

### 2.2 Characterizations

The Rutherford Back Scattering (RBS) spectra of as-deposited CdS film on glass substrates were obtained by our 3 MV 9SDH2 Tandem Pelletron Accelerator using a 5.0 MeV $He^{2+}$ beam for bulk CdS film and 3.049 MeV $He^{+}$ beam for nanocrystalline CdS film. Pure In, Se, Ag, and Cd targets were used for energy calibration.

The optical absorption spectra were recorded with a JASCO model 7800 UV/VIS spectrophotometer at room temperature (28 $^0$C) in the wavelength range 300-700 nm. For this, a bare glass plate was put in front of the reference beam while the glass plate with CdS film was placed in front of the sample beam.

Photoelectrochemical solar cells (PESCs) have been fabricated using CdS films deposited on Ti substrate. The electolyte used was 1 M $Na_2SO_3$ prepared in 30 ml Millipore Q plus water and the counter electrode was a Pt plate of 3 $cm^2$ area. The photocurrents and photovoltages were measured under different load conditions with constant intensity of illumination (60 mW $cm^{-2}$) from a tungsten halogen lamp.

## 3. Results and Discussion

### 3.1 RBS analysis

Fig. 1 shows the RBS spectra of the as-deposited CdS films on glass substrates. Here Fig. 1 (a) is for bulk CdS film (deposition time 30 min at 80 $^0$C, 5.0 MeV $He^{2+}$ beam) and Fig. 1 (b) is for nanocrystalline CdS film (deposition time 6 min at 28 $^0$C, 3.049 MeV $He^{+}$ beam). The details of the analysis are as given in Ref. 1. The edge-heights corresponding to different elements present in the deposit are shown in the spectra. The Si,$O_2$, and Ca-edge as seen from the thinner sample (Fig. 1b) are contributions from the glass substrate. It can be seen from the figure, the sharpness of the Cd-peak decreases with increasing time period of deposition. This is due to the thickness and roughness factor of the deposit. Compositional analysis for bulk CdS film indicated the ratio Cd:S=50.4:49.6 and is in good agreement with reported value [1]. For thinner nanocrystalline film, the

composition ratio was Cd:S=60:40, showing sulfur deficiency. Other researchers [15] have also observed the ratio of Cd/S exceeding unity in CdS clusters encapsulated in zeolite.

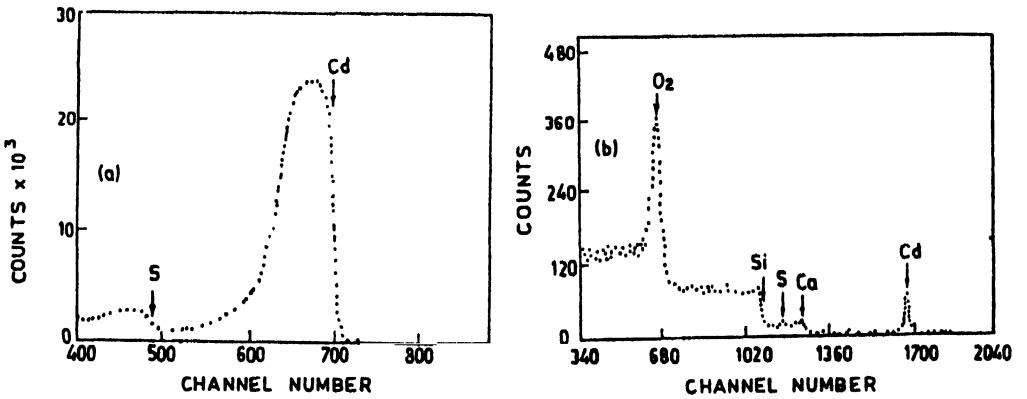


Fig.1: RBS spectra of as-deposited CdS film on glass substrates prepared for (a) 30 min, 80 $^0$C and (b) 6 min, 28 $^0$C. For details see text.

### 3.2 Optical absorption studies

The optical absorption spectra of as-deposited CdS films on glass substrates in the wavelength range 300-700 nm are shown in Fig. 2 for three different samples: 1 (28$^0$C, 6 min); 2 (28$^0$C, 30 min); 3 (80$^0$C, 30 min). From the spectra it is evident that the absorption edge shifts toward lower wavelengths with thinner film. Further our CdS film 1 (Fig. 2) shows absorption peak at 395 nm. Salata et al [10] have also observed such a peak at 395 nm in CdS nanoparticles embedded in polymer system with particle size $\sim$ 45 Å (obtained from transmission electron microscopy (TEM) studies). A similar peak has also been observed by Hoyer et al [17] at 400 nm in CdS quantum-size particles in Au membrane with particle size $\sim$ 50 Å (TEM studies). This peak is due to 1S$-$1S quantum particle transition. A shoulder around 460 nm is also observed by us like in Ref. 17. Our absorption spectrum shows another shoulder at 610 nm. No such features are found in CdS bulk crystallites (CdS film 3, Fig. 2). These observations show that we have most likely obtained particle size between 45 and 50 Å. It is however planned to determine particle size by TEM or X-ray diffraction (XRD) analysis.

CdS is a direct band gap semiconductor, so the absorption coefficient, $\alpha$, can be correlated to the photon energy, $h\nu$, as

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu}.$$

Therefore the band gap, $E_g$, can be found out from the $(\alpha h\nu)^2$ versus $h\nu$ plot (see Fig. 3) extrapolated to zero absorption. The plots are shown for four different

CdS films:1 (2 min, 28$^0$C, 2.99 eV); 2 (6 min, 28$^0$C, 2.97 eV); 3 (30 min, 28$^0$C, 2.65 eV); 4 (30 min, 80$^0$C, 2.40 eV). Thus the band gap changes from 2.40 eV for bulk CdS film to 2.99 eV for nanocrystalline CdS film with decreasing time period of deposition and these are in good agreement with values available in literature.

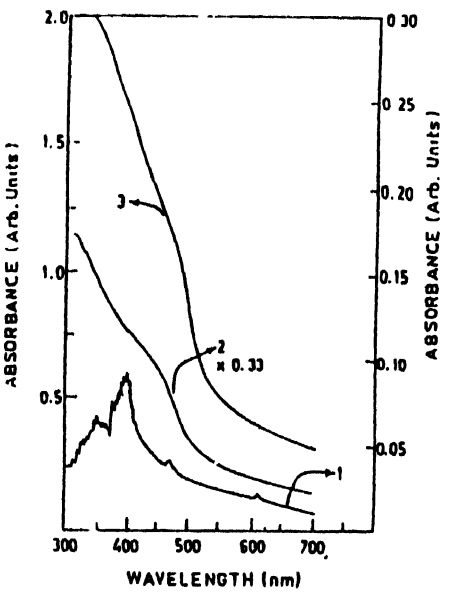


Fig. 2: Optical absorption spectra of as-deposited CdS film (1) 6 min, 28 $^0$C; (2) 30 min, 28 $^0$C; (3) 30 min, 80 $^0$C.

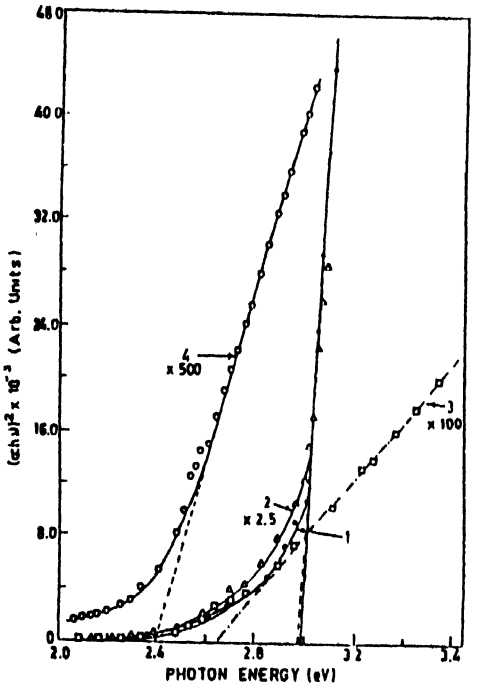


Fig. 3: $(\alpha h\nu)^2$ versus photon energy plot of CdS film; $\alpha$ is the absorption coefficient (arb. units) and $h\nu$ is the photon energy (eV). For details see text.

### 3.3 Photoactivity tests

Photoelectrochemical solar cells (PESCs) with cofiguration Ti/CdS/$Na_2SO_3$/Pt have been fabricated. The open-circuit photovoltages ($V_{oc}$) and short-circuit photocurrents ($J_{sc}$) for different CdS films obtained with constant intensity of illumination (60 mW/cm$^2$) are given in Table I. The PESC performance as seen from the photocurrent versus photovoltage curves (not shown here) is poor and the cells are highly resistive.

Table I. Photoactivity tests using $Na_2SO_3$ electrolyte with solar cell configuration: Ti/CdS/$Na_2SO_3$/Pt. Light intensity: 60 mW/cm$^2$.

| Dep. Temp. $^0$C | Time (min.) | $V_{oc}$ (mV) | $J_{sc}$ $\mu$A/cm$^2$ |
|---|---|---|---|
| 80 | 30 | 580 | 440 |
| 28 | 90 | 652 | 430 |
| 28 | 30 | 677 | 460 |
| 28 | 6 | 681 | 460 |

## 4. Conclusions

A solution growth technique has been used for preparing polycrystalline and nanocrystalline CdS films and a comparative study has been made. RBS compositional analysis showed sulfur deficiency with Cd/S ratio as 50.4/49.6 (bulk) and 60/40 (nano). Optical absorption studies gave the band gap value as 2.40 eV (bulk) and 2.99 eV (nano). Photoelectrochemical solar cells were fabricated using $Na_2SO_3$ electrolyte which gave $V_{oc}$ and $J_{sc}$, respectively, as 580 mV, 440 $\mu$A/cm$^2$ (bulk); and 681 mV, 460 $\mu$A/cm$^2$ (nano).

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